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CONTRACT NO. N00014-86-K-0772

TECHNICAL REPORT NO. 10

Mesogenic Properties of 2',3''''-dimethyl-p-sexiphenyl

by

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Prepared for Publication

in

Molecular Crystals and Liquid Crystals

July 13, 1988

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REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION Unclassified		1d RESTRICTIVE MARKINGS None	
2a SECURITY CLASSIFICATION AUTHORITY		3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public Release, Distribution Unlimited	
2b DECLASSIFICATION/DOWNGRADING SCHEDULE			
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 10		5 MONITORING ORGANIZATION REPORT NUMBER(S)	
6a NAME OF PERFORMING ORGANIZATION University of Connecticut	6b OFFICE SYMBOL (if applicable) ONR	7a NAME OF MONITORING ORGANIZATION Office of Naval Research	
6c ADDRESS (City, State, and ZIP Code) Storrs, CT 06268		7b ADDRESS (City, State, and ZIP Code) 800 North Quincy Avenue Arlington, VA 22217	
8a NAME OF FUNDING/SPONSORING ORGANIZATION	8b OFFICE SYMBOL (if applicable) ONR	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-86-K-0772	
8c ADDRESS (City, State, and ZIP Code) 800 North Quincy Avenue Arlington, VA 22217		10 SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO PROJECT NO TASK NO WORK UNIT ACCESSION NO	
11 TITLE (Include Security Classification) Mesogenic Properties of 2',3''''-dimethyl-p-sexiphenyl (Unclassified)			
12 PERSONAL AUTHOR(S) Girija Subramanian and R. K. Gilpin			
13a TYPE OF REPORT Technical, Interim	13b TIME COVERED FROM _____ TO 07/11/88	14 DATE OF REPORT (Year, Month, Day) 1988-07-11	15 PAGE COUNT 27
16 SUPPLEMENTARY NOTE ON Submitted to Molecular Crystals and Liquid Crystals Research carried out at Kent State University (Subcontractor) (LCPRC Publication No.			
17 COSATI CODES		18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB GROUP	
19 ABSTRACT (Continue on reverse if necessary and identify by block number)			
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20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21 ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a NAME OF RESPONSIBLE INDIVIDUAL Dr. Kenneth J. Hynne		22b TELEPHONE (Include Area Code) (202) 696-4410	22c OFFICE SYMBOL ONR

Mesogenic Properties of
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Abstract

The mesogenic properties of 2',3''''-dimethyl-p-sexiphenyl, 2, have been investigated. Although three endothermic transitions were observed only two were reproducible and correspond to a crystal to crystal change and a crystal to nematic change. A larger than expected decrease in the on-set temperature for the nematic transition and the absence of a smectic transition in 2 compared to p-sexiphenyl, 1, have been observed. These data support a proposed "lock-key" model for molecular conformation of the parent compound, 1 which is not present in 2.

Introduction

p-oligophenlenes have high melting points, good stability, low solubility, and the capacity to fluoresce. They are important as moderators in nuclear reactors, solid and liquid scintillators, and as optical brighteners for electrooptical displays. Additionally, some of these compounds have been shown to have mesogenic properties.

Previously Lewis and Kovac [1] have studied the thermal behavior of p-sexiphenyl, 1, and found that it undergoes two phases changes, a crystal to smectic A transition and a smectic A to nematic transition. The smectic A mesophase was unique in that it did not conform to McMillan's theory [2]. To our knowledge the liquid crystalline properties of laterally substituted p-oligophenlenes have not been reported. In an effort to characterize their behavior and to understand smectic A ordering in 1, the mesogenic properties of 2',3''''-dimethyl-p-sexiphenyl, 2, have been studied.

Experimental Section

The compound 2',3''''-dimethyl-p-sexiphenyl was synthesized by the multi-step sequence shown in reactions 1-7. Details of the procedure are given elsewhere [3].

The microscopic studies were made on a Leitz-Wetzler Ortholux polarizing instrument filled with a modified Mettler FP-2 heating stage. Triplicate determinations were carried out at a heating rate of 2 °C/min. Photographs were taken using a Leitz microscopic 35mm camera and Kodak Kodachrome film (25 ASA). The DSC measurements were performed using either a Perkin Elmer Model DSC-2 differential scanning calorimeter or a Du Pont Model 9900 thermal analyzer equipped with a DSC attachment and pressure cell. Heating rates of 2 and 20 °C/min were used for the DSC scans carried out at ambient pressure. Nitrogen was used as the purge gas. The elevated pressures measurements were under 500 psi of argon at 50 °C/min.

Results

The thermal behavior of 2 was studied by polarized microscopy and differential scanning calorimetry (DSC). Although three endothermic transitions were observed, only two were reproducible.

Microscopy: On heating 2, two phase changes were observed: a crystal to crystal transition at 197 ± 1.1 °C and a crystal to nematic transition at 263 ± 0.3 °C. The nematic nature of the latter transition was confirmed by a characteristic Schlieren pattern (figure 1). The nematic phase persisted up to the thermal limit of the hot stage being used, 300 °C. Replicate studies were carried out and both transitions were reproducible within normal experimental limits. However, during cooling only the higher endothermic change, the nematic to crystal transition, was detected.

Differential Scanning Calorimetry: The transitions detected by microscopy also were confirmed by DSC (figure 2). Their on-set temperatures [and heats of transition] were 196.7 ± 0.9 °C [25.3 ± 0.3 J/g] and 260.3 ± 0.1 [95.1 ± 1.6 J/g]. In addition to these changes, a small exothermic peak (350 °C) and a large endothermic peak (480-580 °C) were observed in the thermogram. These could not be studied by microscopy due to upper heating limitations of our equipment. Although both of the lower temperature endothermic transitions were reproducible, the changes noted at higher temperature were not. These latter transition are believed to be due to decomposition as indicated

by their width, a drifting baseline and the formation of a yellow color which was noted when the sample pans were opened and examined. The extent of decomposition (i.e., variations in the thermograms above 300 °C) varied even under identical heating rates. In an effort to minimize the effect of decomposition on the thermogram a fast heating rate (50 °C/min) and elevated pressure (500 psi) were used. A representative DSC scan is shown in figure 3. Even under these conditions the thermograms obtained at higher temperature were not reproducible.

Discussion

The parent compound, p-sexiphenyl, exhibits two mesophase transitions, a change from the crystal to smectic A form at 435 °C and a change from the smectic A to nematic form at 470 °C [1]. However, in the current study substitution of two lateral methyl groups completely eliminated the smectic mesophase and only a crystal to nematic transition was observed. This behavior is consistent with previous studies of the effect of substitution of identical di, tri, and tetra-lateral groups on the mesomorphic properties of biphenyl analogs [4,5]. Such substitutions have been shown to have an additive influence. In the case of di-substitution interplanar twisting usually alters the close packing of rod like molecules to the extent that smectic properties are eliminated and the on-set temperature of the nematic phase is significantly decreased.

On the basis of this additive substituent principle, the maximum decrease expected for the nematic transition for 2',3''''-dimethyl-p-sexiphenyl is approximately 170 degrees. The actual decrease observed was about 205 degrees which seems unusually large based on simple steric considerations. The substitution of methyl groups in sexiphenyl should not introduce new non-planarity between the phenyl rings which are already out of plane and are conjugated little [4]. Although the interplanar angle is probably increased, this increase would not be expected to be as significant as cases where methyl substitution introduces non-planarity into planar molecules.

The unique features responsible for the transition in 1 may well explain the loss of smectic behavior and the large decrease in the on-set temperature for the nematic transition upon substitution as was noted for 2. Although the polarizability of the phenyl rings and the resulting high intermolecular attraction in polyphenylenes favor parallel alignment, for the compounds to exhibit smectic behavior a minimum value of polarizability is necessary which is present in six ring systems. This minimum value is supported by the fact that p-quinquephenyl, does not exhibit smectic properties [7].

p-sexiphenyl can have two possible parallel alignments as shown in figure 4. These are arbitrarily referred to as head-head (figure 4a) and head-tail (figure 4b) arrangements. Although an assumed interplanar angle of 90 degrees is presented for illustrative purposes, this same two arrangements are possible irrespective of the angle as long as it is greater than zero. In the head-head arrangement, the molecular axes are aligned parallel with the phenyl rings lying in the same plane whereas in the head-tail arrangement, the phenyl are in non-parallel planes (i.e., perpendicular for an interplanar angle of 90 degrees). This latter arrangement gives a better steric ("lock-key") fit for close packing while minimizing pi-electrons repulsion between rings.

The above "lock-key" model explains the high on-set temperature for the smectic transition in p-sexiphenyl as well the large influence of lateral methyl substitution on the liquid crystalline properties of 2. In substituted derivatives of 1 the

intermolecular distance between molecules is increased enough to eliminate advantages of a head-tail arrangement over the head-head configuration. With this increased spacing between molecules, attractive forces are diminished below the threshold value needed for smectic ordering. This model can be verified by additional studies of the liquid crystalline behavior of higher homologues of p-polyphenylenes.

References

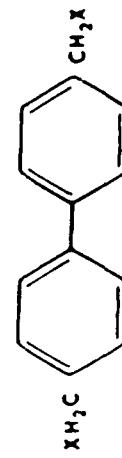
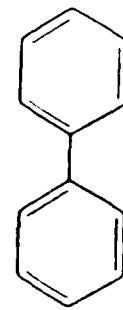
1. I. C. Lewis and C. A. Kovac, Mol. Crys. Liq. Crys., 51, 173 (1979).
2. W. L. McMillan, Phys. Rev., 4, 1238 (1971).
3. G. Subramaniam and R. K. Gilpin, J. Org. Chem., submitted.
4. G. W. Gray, Mol. Crys. Liq. Crys., 7, 127 (1969).
5. D. J. Byron, G. W. Gray and B. M. Worrall, J. Chem. Soc., 3706 (1965).
6. Polycyclic Hydrocarbons, (Edited by E. Clar), Academic Press, New York, NY, 1964, Vol. 11, pp 291.
7. D. Vorlander, Z. Phys. Chem., 4, 1238 (1971).

Reaction Scheme

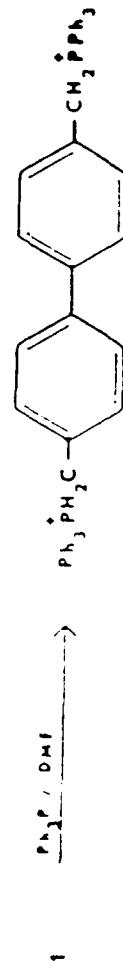
Step 1-7 Preparation of 2',3''''-dimethyl-p-sexiphenyl.

REACTION SCHEME

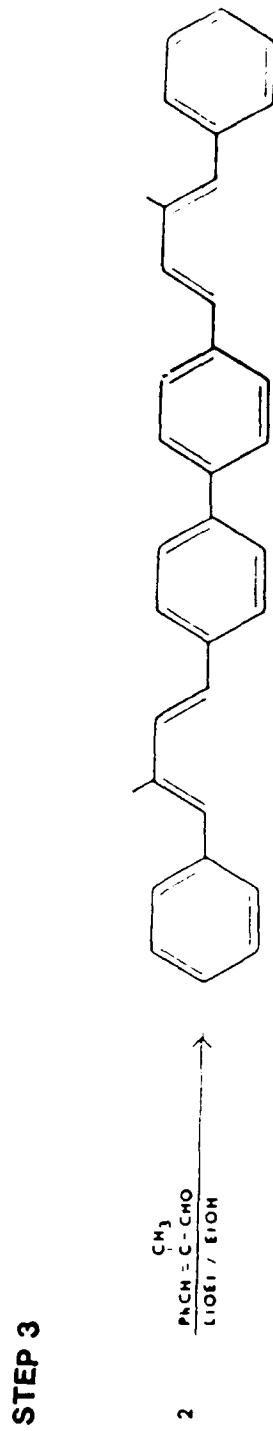
STEP 1

1. $\text{X} = \text{Cl}$ 1. $\text{X} = \text{Br}$

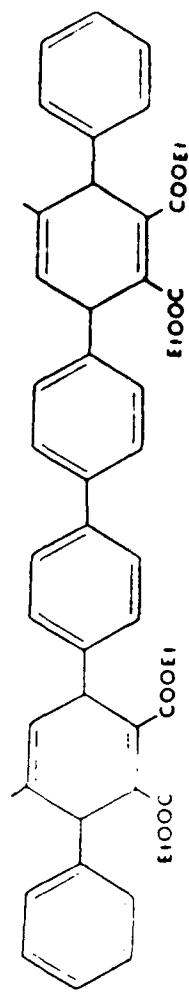
STEP 2



2 X = Cl⁻
2a X = Br⁻



STEP 3

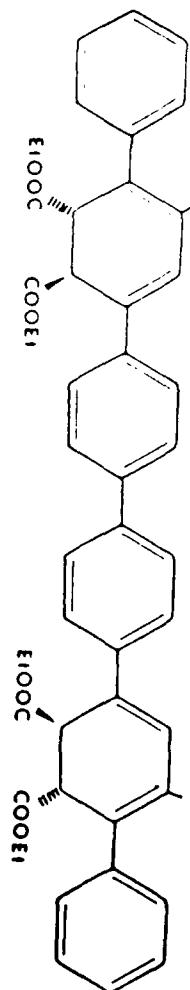


STEP 4

3 DEAD / PHENOL

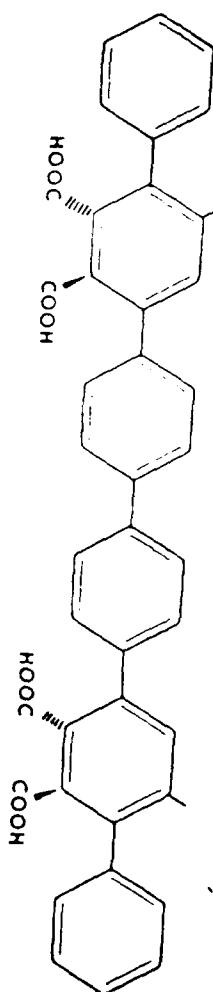
STEP 5

KOH / NaOH
Warm

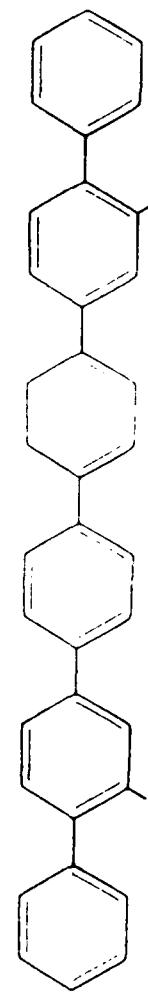


STEP 6

5 → reflux / 24h



STEP 7



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- Figure 1. Photomicrograph illustrating the Schlieren texture of the nematic phase of 2.
- Figure 2. DSC thermogram of 2 obtained at a heating rate of 20 °C/min and at ambient pressure.
- Figure 3. DSC thermogram of 2 obtained at a heating rate of 50 °C/min and at 500 psi of argon.
- Figure 4. Model arrangement of 1: a) head-head configuration, b) head-tail configuration.

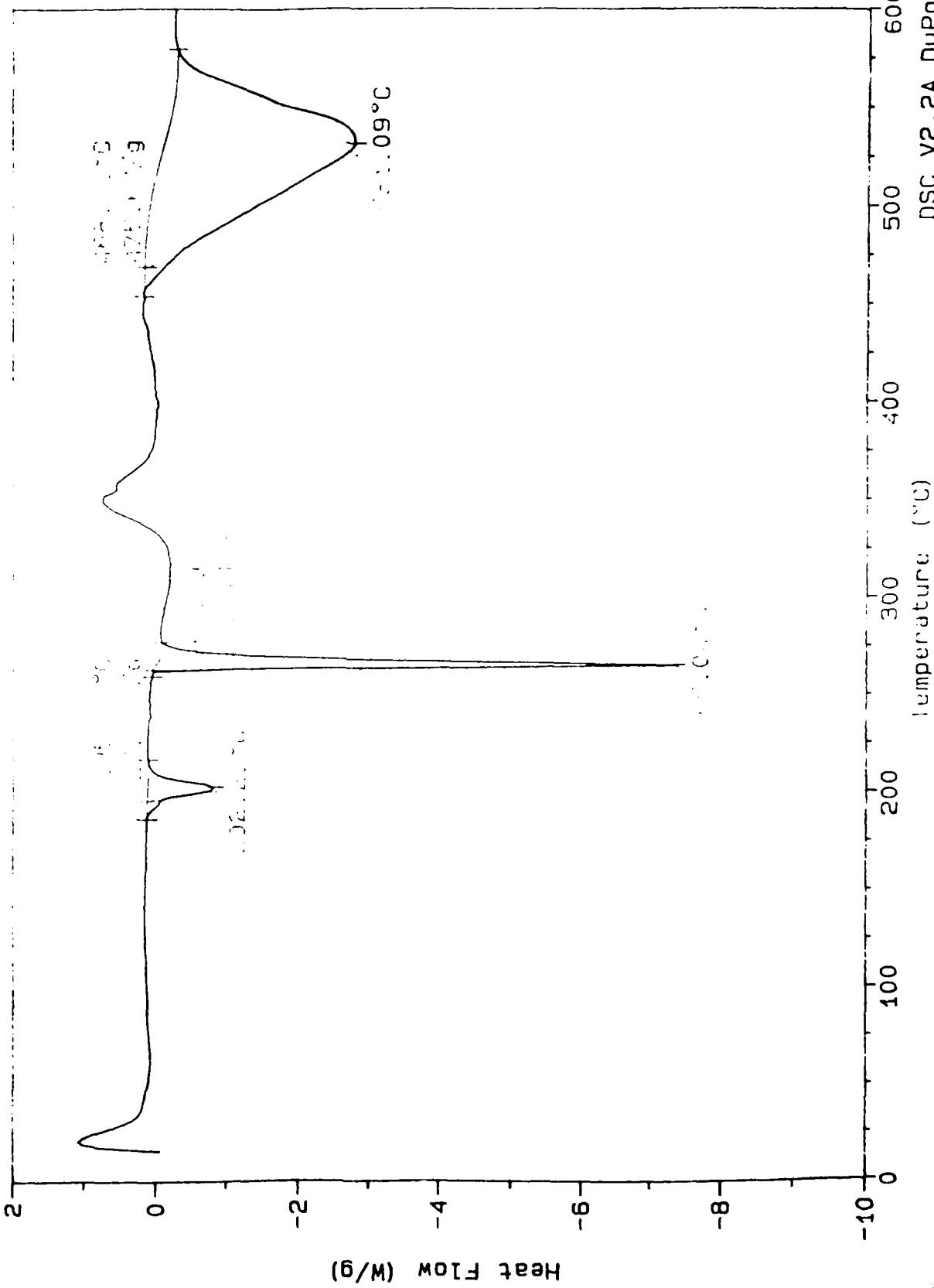


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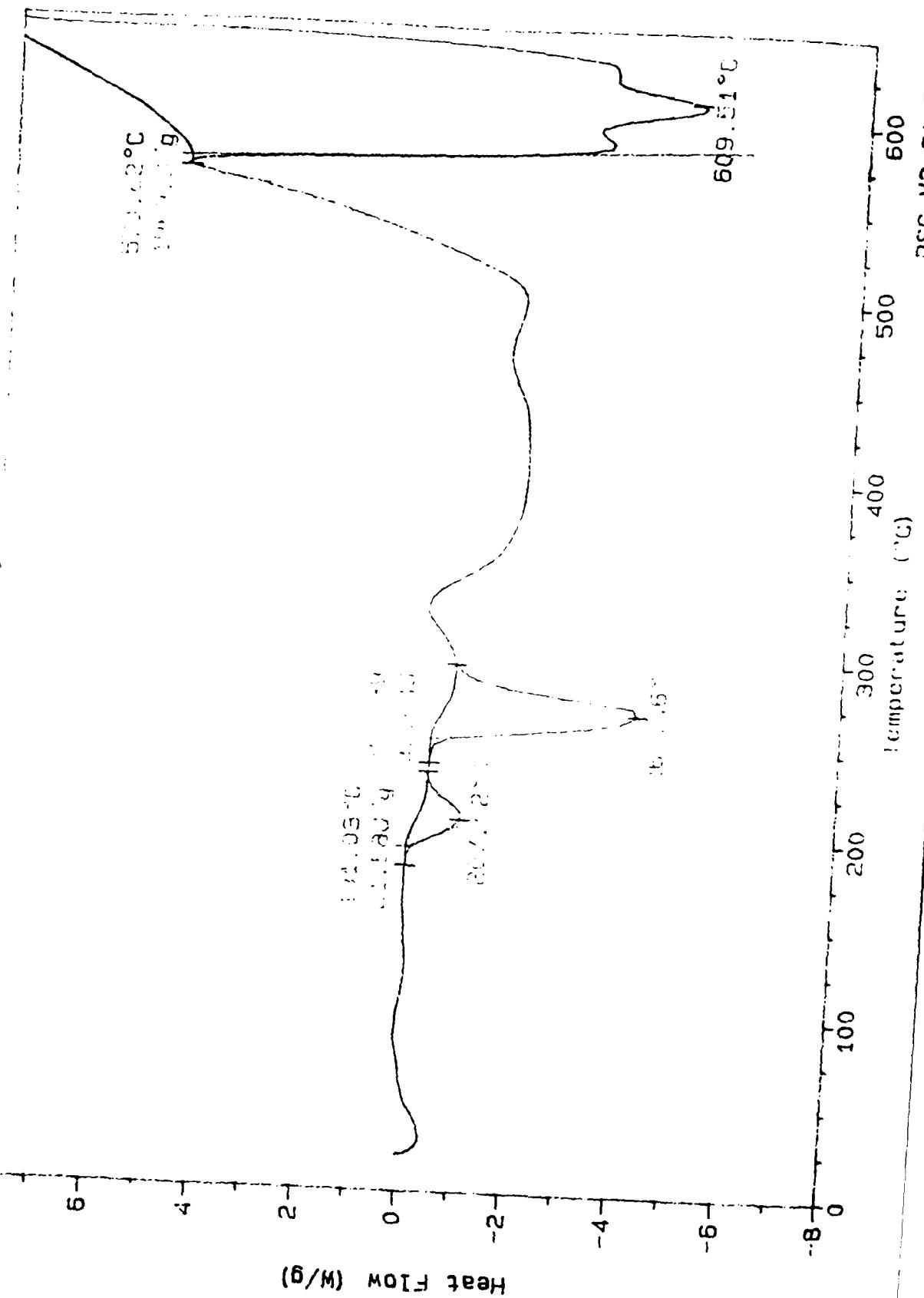
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Sample: DMSP SG-1-45
Size: 1.0570 mg
Method: 20 °C TO 625 °C
Comment: ARGON 100ML/MIN AL PAN



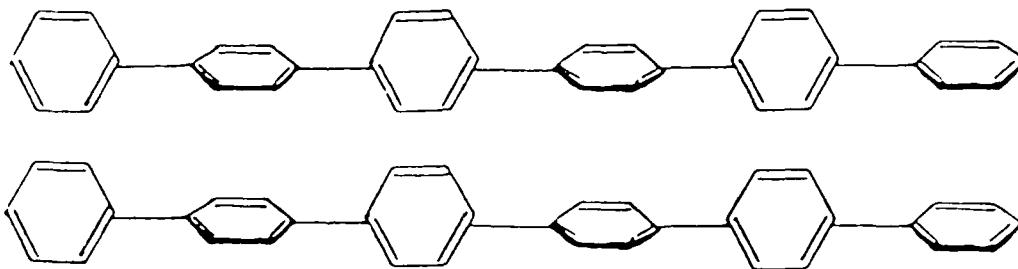
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Sample: SEXIPHENYL
Size: 3.4650 mg
Method: 50 °C/MIN TO 625 °C DSC
Comment: ARGON PRESSURE 500 PSI AL PAN
8

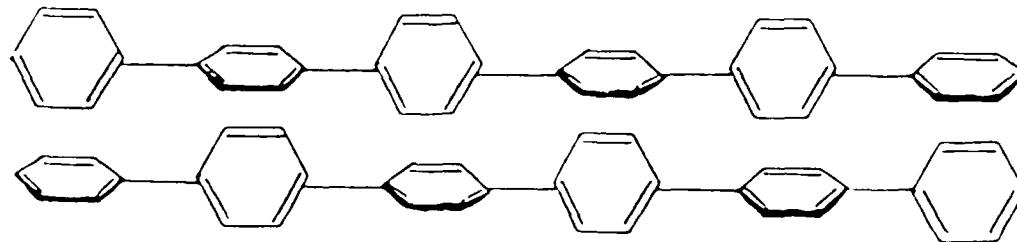


DSC V2.2A DuPont 9500

Head-Head Arrangement of 2



Head-Tail Arrangement of 2



ACKNOWLEDGEMENT

Support from DARPA-ONR Contract N0014-86-K-0772 is
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